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Broadband near-infrared quantum-cutting by cooperative energy transfer in Yb³⁺–Bi³⁺ co-doped CaTiO₃ for solar cells



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ABSTRACT

An efficient near-infrared (NIR) quantum-cutting (QC) process which converts broadband ultravioletblue into NIR via downconversion (DC) has been demonstrated in CaTiO₃:Yb³⁺,Bi³⁺ phosphors for the first time. These phosphors are valuable for use in crystalline Si (c-Si) solar cells, because they efficiently convert 300–480 nm light that is not fully utilized by existing c-Si solar cells into ~1000 nm NIR light that can be sufficiently absorbed by solar cells. Co-doping with 15% Bi³⁺ ions, a significant enhancement in Yb³⁺ NIR integrated emission intensity by a factor of 10 is realized. The phosphors were characterized with the photoluminescence excitation (PLE) and the photoluminescence (PL) spectra evidence the presence of energy transfer (ET) processes from Bi³⁺-related charge transfer state to Yb³⁺ ions. The dependence of Yb³⁺ luminescent intensity on the excitation power was also measured and it demonstrates that the ET processes involve cooperative energy transfer (CET) via two photons QC processes.

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1. Introduction

Solar spectral downconversion (DC) of one ultraviolet-visible (UV-Vis) photon with high energy into two or more near-infrared (NIR) photons with low energy has been proposed as a potential route to get over the spectral mismatch for solar cells [1–3]. A recent quantum-cutting (QC) model proposed by Trupke's team showed a solar cell, modified with a DC layer on the front surface, could achieve a conversion efficiency of up to 38.6%, which exceeded the Shockley-Queisser limit of only ~30% for crystalline Si (c-Si) solar cell [4,5]. Yb³⁺ ions have been identified as almost ideal acceptor species for this purpose, as they have a single excited state ${}^{2}F_{5/2}$ (~10,000 cm⁻¹) above the ground state ${}^{2}F_{7/2}$. The absence of other energy levels allows Yb³⁺ ions to exclusively 'pick up' energy packages of 10,000 cm⁻¹ from other emitted photons to emit \sim 1000 nm photons [6] which are exactly in the most efficient spectral band for c-Si solar cells. QC materials based on $Ln^{3+}-Yb^{3+}$ (Ln = Tb, Tm, Pr, Nd, Ho, and Dy) [6–15] co-doped systems have been considerably researched. However, these NIR materials are still far from practical application because of their narrow excitation band with low excitation efficiency. Recently, much attentions have been paid to broadband NIR OC through host sensitization [16] or co-doping Ce³⁺, Eu²⁺, Yb²⁺, Li+ and Bi³⁺ with strong absorption intensity in the ultraviolet-blue region as energy

donors for Yb³⁺ ions [17–23]. However, most of them still suffer from relative narrow excitation bandwidth. In addition, their excitation peaks mainly locate in 300–350 nm which is much weaker in sunlight radiation, while the blue–green light which is the most intensive part of incident sunlight is not available for conversion into NIR photons. Therefore, novel QC phosphors with broader and redder absorption bands would be desirable for improving the performance of silicon-based solar cells.

Herein, CaTiO₃:Yb³⁺,Bi³⁺, a novel broadband NIR QC phosphor with better adapting to the NIR QC material for c-Si solar cells, is reported for the first time. The broadband energy transfer (ET) from Bi³⁺-related charge transfer (CT) state to Yb³⁺ in CaTiO₃ phosphors was demonstrated by cooperative energy transfer (CET). The CaTiO₃:Yb³⁺,Bi³⁺ phosphor may be incorporated into transparent polymer sheets or prepared in thin film form as luminescent DC layers in front of c-Si solar cells to improve the performance of solar cells.

2. Experimental

The Ca_{0.97-x}TiO₃:3%Yb³⁺*x*%Bi³⁺ (*x* = 0–25%) samples were synthesized by solidstate reaction: stoichiometric amounts of CaCO₃ (AR), TiO₂ (AR), Bi₂O₃ (AR) and Yb₂O₃ (99.99%) were mixed, ground with ethanol, and prefired at 800 °C for 2 h in air. After that the powder was finely ground again, and calcined at 1350 °C for another 2 h in air.

Structure and the phase purity of the as-prepared samples were determined with a Rigaku, D/max-rB analysis (Cu Ka radiation operated at 36 kV and 20 mA, λ = 1.5406 Å, scanning speed 8°/min). The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured with a fiber



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spectrophotometer (AvaSpec-2048TEC-FT, Avantes). The excitation source was a 150 W Xenon lamp equipped with an Omni- λ 300 monochromator (Zolix, Beijing). The dependence of Vb³⁺ luminescence intensity on the excitation power was measured with a laser powermeter (LP-3A, Physcience Opto-Electronics, Beijing) with a 405 nm laser diode as the excitation source. Diffuse reflectance (DR) spectra were performed by a UV–Vis–NIR spectrophotometer (Cary 5000, Varian).

3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) patterns of the as-prepared samples. The results indicate that all patterns of samples except CaTiO₃:3%Yb³⁺,25%Bi³⁺ are consistent with the Joint Committee on Powder Diffraction Standards (JCPDS) Card No. 42-0423 with a space group of Pnma. There is no diffraction peak corresponding to any impurity or allotropic phase, indicating that a pure crystalline compound was obtained at low concentration of Bi³⁺ ions. The ionic radius of Yb³⁺ (0.985 Å) [24] and Bi³⁺ (1.17 Å) [24] is close to that of Ca²⁺ (1.12 Å) [24], therefore, Yb³⁺ and Bi³⁺ ions are believed to substitute the Ca²⁺ sites with little defect. However, an impurity phase corresponding to Bi₂Ti₂O₇ is detected when the concentration of Bi³⁺ ions is up to 25%.

PLE and PL spectra of CaTiO₃:3%Yb³⁺ and CaTiO₃:3%Yb³⁺,15%Bi³⁺ are shown in Fig. 2(a). The PLE spectra show a broadband centered at ~400 nm spanning the spectral range of 300–480 nm for Yb³⁺- doped sample. According to Jørgensen formula [25] the estimated position of the CT band position can be expressed as:

$$\sigma = \left[\chi_{opt}(X) - \chi_{uncorr}(M) \right] 30 \times 10^3 \text{ cm}^{-1}$$
 (1)

where σ is the energy of the CT band, $\chi_{opt}(X)$ is the optical electronegativity of the ligand anion, which is approximately the Pauling's electronegativity, and $\chi_{uncorr}(M)$ is the optical electronegativity of the central metal ion. Taking, $\chi_{opt}(O) = 3.2$ and $\chi_{uncorr}(Yb^{3+}) = 1.68$ [26], the energy of the 2p $(O^{2-}) \rightarrow 4f(Yb^{3+})$ CT band is estimated as 45,600 cm⁻¹ which is near 219 nm and cannot contribute to the broadband. Boutinaud [27] reported the 2p $(O^{2-}) \rightarrow 3d$ (Ti⁴⁺) charge transfer transition within the [TiO₆] octahedral units at about 335 nm. This CT band may be one component of the broad excitation band but not the main peak. In addition, in view of the synthetic method in this study, this broad excitation band seems unlikely resulted from ET processes from various defect levels to Yb³⁺ ions. Therefore, it seems plausible that this broadband may be caused by the absorbance of impurity ions [28] and simultaneously transfer energy to Yb³⁺ in CaTiO₃:Yb³⁺, bringing about NIR emission and corresponding excitation band.



Fig. 1. XRD patterns of samples. The "*" belongs to $Bi_2Ti_2O_7$ impurity phase. The standard data for CaTiO₃ (JCPDS No. 42-0423) is shown as reference.



Fig. 2. (a) PLE and PL spectra of CaTiO₃:3%Yb³⁺ (dash line, black) and CaTiO₃:3%Yb³⁺,15%Bi³⁺ (solid line, red); (b) the dependence of the intensity of NIR emission on the concentration of Bi³⁺ ions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Co-doped with Bi³⁺ ions, the UV-Vis excitation efficiency was greatly enhanced throughout the broadband, especially in the range of 300–460 nm. As is shown in Fig. 2(b), the NIR integrated emission intensity increases by a factor of 10 with the concentration of Bi³⁺ ions up to 15%, which indicates that ET processes from Bi³⁺-related state to Yb³⁺ occurred. Recently, transition metals such as Cr³⁺, Mn²⁺ [29,30] and divalent rare earth Yb²⁺ [20], with Yb³⁺/Nd³⁺ coactivated phosphors have been developed as broadband spectral convertors for improving conversion efficiency of c-Si solar cell. CaTiO₃:Yb³⁺,Bi³⁺ has a really broad PLE spectra which make these phosphors particularly attractive as luminescent DC materials for improving c-Si solar cell performance. Heavily co-doping with 25% Bi³⁺ resulted in a decrease of NIR emission intensity, which might be aroused from the presence of impurity phase (Fig 1). Although the PLE spectra of both CaTiO₃:Yb³⁺,Bi³⁺ and CaTiO₃:Yb³⁺ cover the same region, a significant enhancement of excitation band in CaTiO₃:Yb³⁺,Bi³⁺ is only in the low wavelength range from 300 to 460 nm rather than the whole band. That reflects that different excitation mechanism leads to the additional PL intensity after codoping with Bi3+ ions in CaTiO3:Yb3+. In addition, it has been reported that ultraviolet to bluish-green emission bands were usually observed in Bi^{3+} -doped phosphors due to Bi^{3+} : ${}^{3}P_{1} \rightarrow {}^{1}S_{0}$ transition [22,31]. However, no detectable visible emission was observed both in CaTiO₃:Bi³⁺ and CaTiO₃:Bi³⁺,Yb³⁺. A yellow luminescence of CaTiO₃:Bi³⁺ at 77 K has been reported and ascribed to the transition from Bi³⁺–Ti⁴⁺ metal-to-metal charge transfer state (BT-MMCTs, ~27,000 cm⁻¹) [27]. The position and the profile of reported BT-MMCTs were similar to those of the PLE band of CaTiO₃:Yb³⁺,Bi³⁺ samples. Therefore, the BT-MMCTs rather than Bi³⁺:³P₁ in CaTiO₃:Yb³⁺,Bi³⁺ is inferred to be responsible for transfer energy to ²F_{5/2} level of Yb³⁺ and give rise to a significant enhancement in the intensity of Yb³⁺:²F_{5/2} \rightarrow ²F_{7/2} emission. Similar ET processes in Bi³⁺ co-doped systems from Bi³⁺-related MMCTs to activators have been suggested in Eu³⁺, Pr³⁺ and Yb³⁺ emissions [22,27]. For the first time, we report this ET process from BT-MMCTs to Yb³⁺ in CaTiO₃.

The DR spectra of the samples were shown in Fig. 3. Bands at 335 nm for undoped and Yb³⁺-doped CaTiO₃ were due to the band gap of CaTiO₃, which essentially agreed with previous reports [27,28]. Undoped CaTiO₃ exhibited relatively high absorption in the visible range attributed to the absorption of impurities [28], supporting the assumption for the existence of impurity ions. Bi³⁺ ions have been proven to be an excellent sensitizer for Eu³⁺ and Pr³⁺ ions in CaTiO₃ host with not only enhancing luminescent intensity but also broadening absorption band [32,33]. Co-doping with Bi³⁺ ions, the sample showed a wider and stronger absorption extended to 390 nm, close to the excitation peak of CaTiO₃:Yb³⁺,Bi³⁺ at 400 nm in PLE spectra.

The ET processes in the studied system could be taken through different pathways, such as multiphonon-assisted first-order process and second-order cooperative DC process. The energy mismatch (ΔE) between the lowest energy of BT-MMCTs (22,000 cm⁻¹) and the ${}^{2}F_{5/2}$ level of Yb³⁺ (10,000 cm⁻¹) in CaTiO₃ is approximately 12,000 cm⁻¹, which is far larger than the maximum phonon energy of CaTiO₃ (639 cm⁻¹) [34]. The non-resonant ET combined with phonon assistance is expressed as [35]:

$$K_{PAT}(\Delta E) = {\binom{n+1}{n}}^{N} K_{PAT}(\mathbf{0}) e^{-\beta \Delta E}$$
⁽²⁾

where β is the electron–phonon coupling parameter and $N = \Delta E / \hbar \omega_{max}$, and $\hbar \omega_{max}$ is the maximum phonon energy. Based on the energy gap law and experimental results, a rule of thumb predicts that radiative decay and multiphonon relaxation can complete when the gap is five times the phonon energy [20,36]. The process we studied required eighteen phonons to balance the energy gaps, which was inefficient for the ET through multiphonon-assisted first-order process. Therefore, it could be reasonable to deduce a second-order cooperative DC route for ET process from BT-MMCTs to Yb³⁺, in which the energy at the BT-MMCTs was transferred simultaneously to two Yb³⁺ ions then emitted two NIR photons. In order to verify this assumption, the dependence of the NIR emission



Fig. 3. The DR spectra of the as-prepared samples.

intensity on the excitation power was calculated. It is well known that the output luminescent intensity (I) is proportional to the excitation power $I_p: I \propto I_p^n$, where *n* is the absorbed photon numbers per NIR photon emitted, and its value can be obtained from the slope of the fitted line of the plot of Log(I) versus $Log(I_p)$. As shown in Fig. 4, the slope of CaTiO₃:Yb³⁺ is 0.80, which indicates the energy transfer is a sublinear process and much closer to a linear process with a slope of 1. The present sublinear dependence was aroused by a dominant linear process combining with a second-order nonlinear one. As discussion in PLE and DR spectra, these processes may be brought about by ET from impurity ions. For example, it was known that ET from Yb²⁺ to Yb³⁺ was via second-order DC process [20] while Cr³⁺ to Yb³⁺ was via a linear downshift process [29]. In spite of that, proof for specific impurity ions in CaTiO₃ systems still has much to further study. Comparing with CaTiO₃:Yb³⁺, the slope of CaTiO₃:Yb³⁺,Bi³⁺ reduces to 0.58, which indicates the energy transfer was also a sublinear process but much closer to a second-order nonlinear DC process with a slope of 0.5. This sublinear process was involved in a dominant second-order nonlinear DC process combined with a minority linear one. Combination of an enhancement of NIR emission intensity after co-doped with Bi³⁺ in CaTiO₃:Yb³⁺, we could know that co-doping with Bi³⁺ ions provided additional DC intensity to raise the percentage of second-order process and achieve the conversion of a more linear process to a more nonlinear one. Therefore, it seems to confirm the assumption that the ET process from BT-MMCTs to Yb³⁺ is a second-order cooperative process. Fig. 5 shows the schematic diagram for the BT-MMCTs to Yb³⁺ CET process in CaTiO₃:Yb³⁺,Bi³⁺. The BT-MMCTs situates at about twice energy of the Yb³⁺:²F_{5/2} level while Yb³⁺ has no other levels up to the UV–Vis region. The CET process of BT-MMCTs \rightarrow Yb³⁺:²F_{5/} $_{2}$ + Yb³⁺:²F_{5/2} could, therefore, be the dominant relaxation route to achieve the Yb³⁺ NIR emission. Upon excitation in the BT-MMCTs, one UV–Vis photon is absorbed by these states and then the energy is efficiently transferred to ${}^{2}F_{5/2}$ levels of two Yb³⁺ ions, leading to two NIR photons emitting corresponding to the Yb³⁺:²F_{5/2} \rightarrow ²F_{7/2} transition. Other ET pathways from BT-MMCTs to Yb³⁺ in the studied system have an extremely low probability which could be neglected.

As shown in Fig. 6, the c-Si solar cells work most efficiently in the 950–1100 nm spectral region (Yellow area), but they show weak response to the short-wavelength sunlight (Fig. 6(a)) due to thermal loss, especially in the 300–500 nm where the solar radiation is still strong (Green area). Therefore, DC luminescent materials for c-Si solar cells are expected to convert 300–500 nm light



Fig. 4. Double logarithmic plot of Yb³⁺ emissive intensity in (a) CaTiO₃:3%Yb³⁺ and (b) CaTiO₃:3%Yb³⁺,15%Bi³⁺ versus pump power of the incident 405 nm laser.



Fig. 5. Energy levels and QC mechanism for BT-MMCTs to Yb^{3+} in CaTiO₃: Yb^{3+} , Bi^{3+} . One UV-Vis (300–480 nm) photon absorbed by BT-MMCTs is thereby converted into two ~1000 nm NIR photons.

into NIR emission ~1000 nm for better performance. The CaTiO₃:Yb³⁺,Bi³⁺ developed in the present work matches with this requirement, which can convert 300–480 nm light into NIR emission ~1000 nm. It should be stressed that this excitation band is broadened and the peak position is much closer to the maximum sunlight radiation in current Yb³⁺–Bi³⁺ co-doped DC materials (Table 1) to the best of our knowledge. This process was realized by the second-order DC mechanism. In general, one photon with twofold energy of the c-Si band gap was absorbed by BT-MMCTs, and then the emission of exact the energy of the c-Si solar cell band gap, resulting in a potential improvement in conversion efficiency of solar cells.

4. Conclusion

In summary, a novel broadband NIR QC $CaTiO_3:Yb^{3+},Bi^{3+}$ phosphor has been successfully developed. The results show that $CaTiO_3:Yb^{3+},Bi^{3+}$ could be a deserving material for c-Si solar cells



Fig. 6. Normalized spectral response of a typical c-Si solar cell pyranometer ((a) line with filled dot, brown); UV–Vis PLE spectra ((b) dash line, blue) and NIR PL spectra ((c) solid line, red) of CaTiO₃: Vb³⁺,Bi³⁺. (The cyan background is AM1.5G in UV–Vis–NIR region. The green area is the maximum fraction available for DC, while the yellow area is the maximum response for c-Si solar cells. The data of AM1.5G were reproduced from http://rredc.nrel.gov/solar/spectrum/am1.5/#about). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1

Selected $Yb^{3+}-Bi^{3+}$ couple broadband NIR quantum-cutting materials for c-Si solar cells.

Host lattice	Preparation method	Excitation (nm)	Peak (nm)	Refs.
YVO ₄	Solid-state reaction	250-400	342	[22]
Gd_2O_3	Combustion synthesis	300-400	347	[31]
Y_2O_3	Pulsed laser deposition	300-400	331	[37]
YNbO ₄	Solid-state reaction	250-350	274	[38]
CaTiO ₃	Solid-state reaction	300-480	400	This work

for efficient conversion of 300–480 nm light which was not fully utilized by the existing solar cells to ~1000 nm NIR light. Co-doping with Bi^{3+} ions, an enhancement in Yb^{3+} NIR integrated emission intensity by a factor of 10 was realized, which made this material particularly attractive as a luminescent DC phosphor for improving the performance of silicon-based solar cells. The PLE and PL spectra measurements disclosed the occurrence of ET processes from BT-MMCTs to Yb^{3+} ions. Furthermore, through the study of the dependence of luminescent intensity on the excitation power at RT, it was demonstrated that the ET processes involved CET via two photons quantum cutting processes.

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